



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : A01N 25/12		A1	(11) International Publication Number: WO 93/06723 (43) International Publication Date: 15 April 1993 (15.04.93)
(21) International Application Number: PCT/US92/07804 (22) International Filing Date: 17 September 1992 (17.09.92)			(81) Designated States: AU, BB, BG, BR, CA, CS, FI, HU, JP, KP, KR, LK, MG, MN, MW, NO, PL, RO, RU, SD, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).
(30) Priority data: 771,711 4 October 1991 (04.10.91) US			Published <i>With international search report.</i>
(71) Applicant: OLIN CORPORATION [US/US]; 350 Knotter Drive, P.O. Box 586, Cheshire, CT 06410-0586 (US).			
(72) Inventors: CASBERG, John, M. ; 370 Sycamore Lane, Cheshire, CT 06410 (US). FRENCH, Cheryl, B. ; 817 Hopewell Road, South Glastonbury, CT 06073 (US).			
(74) Agents: CARLSON, Dale, Lynn et al.; Olin Corporation, 350 Knotter Drive, P.O. Box 586, Cheshire, CT 06410-0586 (US).			
(54) Title: FUNGICIDE TABLET			
(57) Abstract A chemical fungicide tablet is disclosed and a method of producing such a tablet and a method of fungicidal treatment of a fluid reservoir through use of the tablet.			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SK	Slovak Republic
CI	Côte d'Ivoire	LK	Sri Lanka	SN	Senegal
CM	Cameroon	LU	Luxembourg	SU	Soviet Union
CS	Czechoslovakia	MC	Monaco	TD	Chad
CZ	Czech Republic	MG	Madagascar	TC	Togo
DE	Germany	ML	Mali	UA	Ukraine
DK	Denmark	MN	Mongolia	US	United States of America
ES	Spain			VN	Viet Nam
FI	Finland				

-1-

"FUNGICIDE TABLET"

This invention relates generally to chemical tablets and, more specifically, to a chemical fungicide tablet and, still more specifically to a sodium pyridine thione tablet, to the method of compressively forming the tablet and to the method of employing that tablet in a fluid reservoir for fungicidal purpose.

Chemical tablets for fluid reservoir bactericidal purpose are known. No chemical fungicide tablet is known for that purpose. One bactericidal tablet is a 10 28.4 gm, 2.0 inch diameter, 0.428 inch high, 1.29 gm/cc density tris(hydroxymethyl) nitromethane known as the "Angus SST Sump Saving Tablet" available commercially from Angus Chemical Company. Sodium pyridine thione ("NaPT") in liquid form is presently used in fluid 15 reservoirs for fungicidal purpose. Solid sodium pyridine thione is not currently available for these applications. Sodium pyridine thione powder is a powerful sternutator (sneeze inducer) and therefore difficult to handle in powder form. While the liquid 20 NaPT is completely water soluble and is highly effective in the proper dosage, measuring liquids for the proper dosing of small reservoirs (10-500 gallons) is difficult for those in charge of maintenance of the fluid reservoirs. The primary type of fluid reservoir 25 involved is a small (10-500 gallon) fluid sump for metalworking equipment and the normal person in charge of the sump is the machinist. Machinists are normally not skilled in bacteriology or chemistry, so proper

-2-

dosing with a liquid dosant can be problematic. Difficulties in measuring small quantities of liquids leads to overdosing and to greater incidence of dermal contact through spilling.

5 These problems are solved in the tablet of the present invention and in the process of making the tablet and in the process of using the tablet by providing a chemical fungicide tablet which dissolves quickly. The dosing problem is solved in that the
10 tablet can be made of a size and composition which achieves the proper dosage (or some specific portion of the dosage if multiple tablets doses are used) and which need not be handled by the machinist or other operator of the fluid reservoir.

15 It is an object of the present invention to provide a fast dissolving fungicidal tablet.

It is a further object of the invention to provide a sodium pyrithione tablet.

It is another object of the present invention to
20 provide a rapidly dissolving sodium pyrithione tablet.

It is an object of the present invention to provide a process for making a chemical fungicide (preferably a sodium pyrithione) tablet that will rapidly dissolve.

25 It is another object of the present invention to provide a method of fungicidal treatment of a fluid reservoir which method uses a rapidly dissolving chemical tablet.

It is a preferred feature of the present
30 invention that the tablet has a moisture content of less than about 7.5% by weight and more preferably within the range of from about 0.25% to about 7.5%.

It is an advantage of the present invention that the tablet is capable of achieving an effective

-3-

dosage within approximately 30 minutes with a tablet surface area of less than 5 square inches.

It is another advantage of the present invention that the tablet is relatively strong, 5 preferably having a compressive yield strength of at least about 90 pounds.

These and other objects, features and advantages are obtained by the tablet and methods of the present invention.

10 The tablet of the invention is preferably a sodium pyridine thione fungicidal chemical tablet. Other fungicides useful in fabricating the tablet include zinc pyrithione; 1,2-benzisothiazolin-3-one; 3-iodo-2-propynyl butyl carbamate; 15 2-bromo-2-nitropropan-1,3-diol; 1,2-dibromo-2,4-dicyanobutane; 2-(4-thiazolyl)-benzimidazole; 2,4,5,6-Tetrachloroisophthalonitrile; 1-imidazoyl-1-(4'-chlorophenoxy)-3,3-dimethylbutan-2- 20 one; 1-hydroxy-4-methyl-6-(2,4,4-trimethylpentyl)-2(1H)-pyridone and salts; 2-(thiocyanomethylthio)benzothiazole and combinations thereof.

25 Preferably the tablet is a fungicidal tablet for fluid reservoir treatment, which tablet comprises compressed granules of sodium pyrithione.

30 The method of manufacturing the tablet is a method of forming a chemical fungicide tablet, which method comprises the steps of:

 (a) introducing a quantity of granular solid chemical fungicide into a tabletting mold, the chemical fungicide granules having a moisture content

-4-

of less than about 7.5% by weight and more preferably within the range of from about 0.25% to about 7.5%;

(b) compressing the introduced granules into a tablet with a density of at least 0.6 gm/cc and
5 more preferably greater than 1.0 gm/cc; and

(c) ejecting the tablet from the die without breaking the tablet.

The method of treatment using the tablet is a method of fungicidal treatment of a fluid reservoir,
10 which method comprises the steps of:

(a) introducing at least one chemical fungicide tablet into the fluid reservoir;

(b) dissolving the introduced tablet in the reservoir fluid at a rate of at least 0.5 grams
15 per minute in order to obtain a fungicidally effective concentration of chemical fungicide in the reservoir.

The chemical fungicide employed in the present invention is sodium pyrithione.

The sodium pyrithione suitably employed in the process of the present invention is a well known commercial product and is commonly made by reacting 2-chloropyridine-N-oxide with NaSH and NaOH, as disclosed in U.S. Patent No. 3,159,640.

The process of making the tablet of the present invention includes the steps of: (a) introducing a quantity of granular chemical fungicide into a tabletting mold, the chemical fungicide granules having a moisture content of less than about 7.5% and preferably within the range of from about 0.25% up to about 7.5% by weight; (b) compressing the introduced granules into a tablet with a density of at least 0.6 gm/cc preferably greater than 1.0 gm/cc;

and (c) ejecting the tablet from the die without breaking the tablet.

The method preferably further comprises the step of coating with a lubricating compound the 5 portion of the tableting mold which is intended to contact the chemical fungicide granules. The lubricating compound is preferably tetrafluoroethylene although any other lubricating compound, such as a stearate compound, which is non-reactive with chemical 10 fungicide and which does not adhere to chemical fungicide can be utilized.

The invention also provides the method of fungicidal treatment of a fluid reservoir, which method comprises the steps of: (a) introducing at 15 least one chemical fungicide tablet into the fluid reservoir; (b) dissolving the introduced tablet in the reservoir fluid at a rate of at least 0.5 grams per minute to obtain a fungicidally effective concentration of chemical fungicide in the reservoir.

20 Metalworking fluids are complex solutions or emulsions of agents designed but not limited to: minimize friction and remove heat; to protect against corrosion; to keep the solution stable; to lubricate and reduce surface tension; to provide 25 extreme-pressure lubrication and to provide microbial protection. The typical ingredients found in metalworking fluid compositions consists of: water; mineral oil; sulfonates; non-ionic, anionic, and cationic surfactants; polyalkylene glycols; fatty acids; carboxylic acid esters; phosphate esters; chlorinated and sulfurized extreme pressure agents; ethanolamines; amine borates; biocides; fragrances; 30 and dyes.

-6-

The preferred fungicide is sodium pyrithione. A 15 gram tablet has been found to be a preferred size to serve as a single tablet dosage for small fluid reservoirs and a suitable size for larger reservoirs, 5 as well, since for larger reservoirs the dosage can be applied by use of multiple tablets. The sodium pyrithione dissolves rapidly in the fluid, normally water, so that a fungicidally effective concentration of 60 ppm is reached within less than 30 minutes. In 10 contrast, the bactericidal 28gm Angus SST tablets noted above must reach a concentration of 600 ppm to be effective as a bactericide. An advantage of sodium pyrithione in the fungicidal treatment of fluid reservoirs is the relatively low concentration that is 15 fungicidally effective.

EXAMPLE 1

A 15 gram quantity of granulated sodium pyrithione of a particle size of the following distribution:

	<u>Particle Size (microns)</u>	<u>Percent</u>
20	>500	40.2
	300-500	09.4
	150-300	13.8
	075-150	18.2
25	038-075	12.6
	<u><038</u>	<u>05.8</u>
	Total.....	100.0

was placed in a one inch diameter tabletting mold cavity of cylindrical shape and compressed with a 30 Carver Model B press at room temperature (about twenty-two degrees Centigrade) and a pressure of 12,700

-7-

psi for a duration of about 1-2 seconds. The particles had a water content of approximately 0.4% and the finished tablet had a water content of approximately 0.4%. The finished tablet had a compressive yield 5 strength (crush strength) of about 105 pounds. The finished sodium pyrithione tablet was placed in a 5 gallon tank of water with one-half gallon per minute circulation in and out of the tank and was found to dissolve at a rate in excess of 15 gm/30 min. An 10 effective fungicidal concentration of 790 ppm (well in excess of the fungicidally effective concentration of 60 ppm) was achieved in less than 30 minutes, indicating satisfactory dissolving rate.

EXAMPLE 2

15 A 15 gram quantity of granulated sodium pyrithione of a particle size of the following distribution:

	<u>Particle Size (microns)</u>	<u>Percent</u>
	>500	22.7
20	300-500	12.1
	150-300	23.1
	075-150	21.5
	038-075	13.4
	<u><038</u>	<u>7.2</u>
25	Total.....	100.0

was placed in a one inch diameter tabletting mold cavity of cylindrical shape and compressed at room temperature (about 22 degrees Centigrade) and a pressure of 12,700 psi for a duration of about 1-2 30 seconds. The particles had a water content of approximately 3.8% and the finished tablet had a water

-8-

content of approximately 3.8%. The finished tablet had a compressive yield strength (crush strength) of >350 pounds.

While the invention has been described above with references to specific embodiments thereof, it is apparent that many changes, modifications and variations in the materials, arrangements of parts and steps can be made without departing from the inventive concept disclosed herein. For example, in employing the tablet of the present invention, the tablet could have any desired shape and size. Accordingly, the spirit and broad scope of the appended claims is intended to embrace all such changes, modifications and variations that may occur to one of skill in the art upon a reading of the disclosure.

WHAT IS CLAIMED IS:

1. A metalworking fluid composition characterized by said composition comprising:
 - (a) a chemical fungicide tablet; and
 - (b) an aqueous metalworking fluid.
2. The composition of Claim 1 characterized in that the fungicide is selected from the group consisting sodium pyrithione, zinc pyrithione; 1,2-benzisothiazolin-3-one; 3-iodo-2-propynyl butyl carbamate; 2-bromo-2-nitropropan-1,3-diol; 1,2-dibromo-2,4-dicyanobutane; 2-(4-thiazolyl)-benzimidazole; 2,4,5,6-Tetrachloroisophthalonitrile; 1-imidazoyl-1-(4'-chlorophenoxy)-3,3-dimethylbutan-2-one; 1-hydroxy-4-methyl-6-(2,4,4-trimethylpentyl)-2(1H)-pyridone and salts; 2-(thiocyanomethylthio)benzothiazole and combinations thereof.
3. The composition of Claim 1 characterized in that the tablet has a moisture content of less than about 7.5% by weight.
4. The composition of Claim 1 characterized in that the tablet has a moisture content within the range of from about 0.25% up to about 7.5% by weight.
- 25 5. The composition of Claim 1 characterized in that the tablet has a moisture content within the range of from about 1.00% up to about 5.0% by weight.

-10-

6. The composition of Claim 1 characterized in that the tablet has a moisture content within the range of from about 1.25% up to about 4.0% by weight.

7. A fungicidal tablet for fluid reservoir
5 treatment characterized in that the tablet comprises compressed granules of chemical fungicide.

8. The tablet of Claim 7 characterized in that the fungicide is sodium pyrithione.

9. The tablet of Claim 7 characterized in
10 that the tablet has interconnected granules and no connective binder other than the chemical fungicide granules themselves.

10. The tablet of Claim 7 characterized in that the tablet has a moisture content less than about
15 7.5% by weight.

11. The tablet of Claim 7 characterized in that the tablet has a moisture content within the range of from about 1.00% up to about 5.0% by weight.

12. The tablet of Claim 7 characterized in
20 that the tablet has a moisture content within the range of from about 1.25% up to about 4.0% by weight.

-11-

13. A method of forming a chemical fungicide tablet characterized by the steps of:

- (a) introducing a quantity of granular chemical fungicide into a tabletting mold, the
5 chemical fungicide granules having a moisture content less than 7.5% by weight;
- (b) compressing the introduced granules into a tablet with a density of at least 0.6 gm/cc; and
- (c) ejecting the tablet from the die
10 without breaking the tablet.

14. The method of Claim 13 characterized in that the chemical fungicide is sodium pyridine thione.

15. The method of Claim 13 characterized in that the tablet is compressed to a density greater
15 than 1.0gm/cc.

16. The method of Claim 13 characterized by the further step of coating with a lubricating compound the portion of the tabletting mold which is intended to contact the chemical fungicide granules.

20 17. The method of Claim 16 characterized in that the lubricating compound is tetrafluoroethylene.

18. The method of Claim 16 characterized in that the lubricating compound is a stearate compound.

-12-

19. A method of fungicidal treatment of a fluid reservoir characterized by the steps of:

(a) introducing at least one chemical fungicide tablet into the fluid reservoir; and

5 (b) dissolving the introduced tablet in the reservoir fluid at a rate of at least 0.5 grams per minute in order to obtain a fungicidally effective concentration of chemical fungicide in the reservoir.

20. An industrial or commercial composition
10 characterized by said composition comprising:

(a) a base fluid; and

(b) a chemical fungicide tablet.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US92/07804

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : A01N 25/12

US CL : 424/408

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/408, 464, 465, 470

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CHEM. ABSTRACTS Vol. 108, 105675a HPLC analysis for sodium 2-pyridinethiol 1-oxide in aqueous metalworking fluids via derivatization with NBD-Cl. (VALDEZ), (1988), entire document.	1-20
Y	EP, A, 0 109 738 (ROHM AND HAAS COMPANY) 30 MAY 1984, entire document.	1,2,7,19,20
Y	US, A, 5,049,385 (WIEDRICH) 17 SEPTEMBER 1991. See entire document	1-20
Y	GB, A, 1,358,915 (MERCK & CO., INC.) 03 JULY 1974, entire document.	1,7,9,13,19

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

09 NOVEMBER 1992

Date of mailing of the international search report

29 DEC 1992

Name and mailing address of the ISA/
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Authorized officer

NEIL LEVY

Levy

Facsimile No. NOT APPLICABLE

Telephone No. (703) 308-2351